FORM PTO-1390 (Modified) (REV 5-93) | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | ATTORNEY'S DOCKET NUMBER 054270/0122

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

514 Rec'd PCT/PTO 22 OCT 1999

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5) 09/403505

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/AU98/00326	6 May 1998	6 May 1997

TITLE OF INVENTION
FABRICATION OF ZINC OXIDE FILMS ON NON-PLANAR SUBSTRATES AND THE USE THEREOF

APPLICANT(S) FOR DO/EO/US
Michael Herman KOCH, Robert Norman LAMB, Peter Yorke TIMBRELL, Gock Leong MAR

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).

4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)

6. ☐ A translation of the International Application into English (35 U.S.C. 371 (c)(2)).

7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.

8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.

14. ☐ A substitute specification.

15. ☐ A change of power of attorney and/or address letter.

16. ☒ Other items or information:

Copy of 1 page of Annexes submitted herewith; Copy of Search Report

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5) 09/403505	INTERNATIONAL APPLICATION NO. PCT/AU98/00326	ATTORNEY'S DOCKET NUMBER 054270/0122

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17. ☒ The following fees are submitted:	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5):		
Search Report has been prepared by the EPO or JPO $840.00	**$840.00**	
International preliminary examination fee paid to USPTO (37 CFR 1.482) $670.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2) $760.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $970.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $96.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ **840.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e))	$ **0.00**	

Claims	Number Filed	Number Extra	Rate		
Total Claims	**15** -20 =	**0**	X **$18.00**	$ **0.00**	
Independent Claims	**4** -3 =	**1**	X **$78.00**	$ **78.00**	
Multiple dependent claim(s) (if applicable)			+ **$260.00**	$ **0.00**	
TOTAL OF ABOVE CALCULATIONS =				$ **918.00**	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$ **0.00**	
SUBTOTAL =				$ **918.00**	
Processing fee of **$130.00** for furnishing English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f). +				$ **0.00**	
TOTAL NATIONAL FEE =				$ **918.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$	
TOTAL FEES ENCLOSED =				$ **918.00**	
				Amount to be: refunded $	
				charged $	

a. ☒ A check in the amount of $918.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 19-0741 in the amount of $ to the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 19-0741. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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S. A. Bent
SIGNATURE

Stephen A. Bent
NAME

29,768
REGISTRATION NUMBER

Form PTO-1390 (REV 5-93) (Modified)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No. 54270/122

In re patent application of
Michael H. KOCH et al.
Serial No. Unassigned
Filed: October 22, 1999
For: FABRICATION OF ZINC OXIDE FILMS ON NON-PLANAR SUBSTRATES AND THE USE THEREOF

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, Applicants respectfully request that the following amendments be entered into the application:

IN THE CLAIMS:

Claim 3, line 1, please delete "or 2";

Claim 4, line 1, please delete "any one of the preceding claims" and insert --claim 1--;

Claim 5, line 1, please delete "any preceedinng claims" and insert --claim 1--;

Claim 6, line 1, please delete "any one of the preceding claims" and insert --claim 1--;

Claim 8, line 1, please delete "any one of the preceding claims" and insert --claim 1--;

Attorney Docket No. 54270/122

Claim 15, line 1, please delete "as claimed in claim 13 or claim 14 including" and insert --that has a phase modulation efficiency greater than substantially 0.25 rad/√FMW/cm and that includes--;

line 4, please delete "any of claims 1 to 11" and insert --claim 1--.

REMARKS

Applicants respectfully request that the foregoing amendments to Claims 3-6, 8 and 15 be entered in order to avoid this application incurring a surcharge for the presence of one or more multiple dependent claims.

Respectfully submitted,

October 22, 1999

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Fabrication of Zinc Oxide Films on Non-Planar Substrates and the Use Thereof

Field of the Invention

The present invention relates to the fabrication of Zinc Oxide films on non-planar substrates such as optical fibres and their use in devices such as piezo-electric or electro optic modulators.

Background of the Invention

Recently, there has been a growing interest in the development of thin film piezo-electric materials for use in all fibre acousto-optic modulators. In Fig.1 there is illustrated a schematic representation of the typical modulator device structure 10 where a film of active material 11 (typical thickness from 5 to several 10's of μm) is sandwiched between two electrical contact layers 12, 13 (thicknesses up to 1μm) covering a full 360° surface of a fibre. The cylindrical geometry of such devices 10 results in highly efficient polarisation independent modulators as the acoustic waves are focussed at the fibre core 15.

The active material 11 can be Zinc Oxide (ZnO) which is a II-VI semiconductor with strong piezo-electric and electro-optic properties ideal for use in compact thin film fibre modulators with frequency responses up to 1GHz. In crystalline zinc oxide, the c-axis is a polar axis due to effective ionic charges between the alternating Zn and O layers. It is therefore important that the ZnO thin film structure is one in which the crystallites are oriented with their c-axis parallel to the applied electric field.

To date ZnO films used in the fabrication of all-fibre modulators have been deposited using various forms of sputtering from a ZnO target. The devices previously constructed have had limited maximum attainable efficiency and phase modulation. Further, with utilising sputtering, rotation of the optical fibre was required due to the

directional nature of the high energy deposition process. This was found to have an undesirable affect on device performance. Further, the most important limiting factor in these devices appears to be the non-negligible conductivity of the deposited films.

Summary of the Invention

It is an object of the present invention to provide for an improved method of fabrication of zinc oxide films on non-planar substrates such as optical fibres of the like. Further, it is an object of the present invention to construct devices utilizing the aforementioned improved films.

In accordance with a first aspect of the present invention, there is provided a method of manufacture of a substantially continuous circumferential coating on a non-planer substrate, the method comprising the steps of:
utilising a substantially non directional deposition technique and a substantially static substrate deposition geometry to deposit the coating.

Coatings can be deposited which include piezo-electric modulation characteritics or electro-optic modulation characteristics. Ideally the coating has semiconducting properties. The type of coating ideally includes Zinc-Oxide coatings.

The non directional deposition technique can comprise chemical vapour deposition via single source chemical vapour deposition.

Suitable substrates include optical fibres which are clamped onto a substantially planar heating surface during the deposition. The optical fibre can be clamped at a portion of the length of the fibre which is located at one end of a heating surface during the deposition such that movement of a free end of the optical fibre is limited to movement substantially along the axis of the optical fibre.

In accordance with a second aspect of the present invention, there is provided a receptacle for an optical

fibre arranged to be used in a method of manufacture of a circumferential coating on an optical fibre utilising a substantially non directional deposition technique and a substantially static substrate deposition geometry, the receptacle comprising: a substantially planar heating surface; a clamping means for clamping the substrate fibre onto the heating surface, wherein the clamping means is arranged to clamp the fibre at a portion of the length of the optical fibre which is located at one end of the heating surface during the manufacture of the coating; and means for limiting a movement of a free end of the optical fibre to movement substantially along axis of the optical fibre.

In accordance with a further aspect of the present invention, there is provided an acusto-optical phase modulator having a phase modulation efficiency greater than substantially 0.25 rad/√FMW/cm and further preferably having a substantially linear relationship between phase modulation and driving power for driving powers greater than 36mW.

It has been found in practice that, through the utilisation of chemical vapour deposition techniques, acusto-optical phase modulators having higher levels of efficiency, in excess of 0.25 radiums/√MW/cms, can be constructed. Further, phase modulators utilising the aforementioned techniques have been found to have substantially higher phase modulation capabilities than previously possible. This allows for their incorporation in interferometric optic arrangements which have improved phase modulation characteristics.

Brief Description of the Drawings

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Fig. 1 is a schematic of a typical thin film acousto-optic fibre phase modulator;

Fig. 2 illustrates a CVD system utilised for the preparation of CVD films in accordance with the preferred embodiment;

Figs. 3a and 3b illustrate a sample holder constructed in accordance with the preferred embodiment;

Fig. 4 illustrates a cross-sectional view of a fibre holder as utilised in the preferred embodiment;

Fig. 5 illustrates the X-ray diffraction spectra of a zinc oxide film as recorded for films deposited in the preferred embodiment;

Fig. 6 illustrates a plot of the depth profile of a CVD zinc oxide film;

Fig. 7 illustrates a plot of X-ray diffraction intensities for ZnO films deposited in accordance with the preferred embodiment;

Fig. 8 illustrates one form of modulator constructed in accordance with the preferred embodiment; and

Fig. 9 illustrates a plot of measured phase modulation verses driving power for various resonant frequencies for devices constructed in accordance with the preferred embodiment and the prior art.

Fig. 10 illustrates a chart of the preferred orientation (or texture) of ZnO films grown as a function of both precursor pressure and substrate temperature; and

Fig. 11a to 11c represents various schematic views of the modified Knudsen cell.

Description of the Preferred and Other Embodiments

In the preferred embodiment, an all-fibre acousto-optic phase modulator was produced using a ZnO film deposited by a modified single source chemical vapour deposition (SSCVD) process from a metal-organic precursor. The precursor used was $Zn_4O(CH_3COO)_6$ (basic zinc acetate, BZA).

In Fig. 2, there is illustrated a schematic of the

high vacuum chamber 20 utilized to construct the modulator. The films were deposited in a high vacuum ($P \leq 1x10^{-6}$mbar), and the BZA precursor 21 was vapourised in a modified Knudsen cell 22 by resistively heating the cell. Fig. 11a to 11c illustrate various views of the modified two zone Knudsen cell which includes a reservoir 110 formed via a screw in stopper 111, an outer cell 112 and a series of bores 114 for the receipt of ceramic insulated Ta resistance wires for heating. Also provided is an exit aperture 115 for the exit of materials.

The cell temperature was adjusted so that the partial pressure of BZA in the chamber 20 was approximately $1x10^{-5}$mbar. The film was deposited onto a heated sample substrate 23 (Fig. 2) heated to 450°C in the presence of a water ambient of $2x10^{-3}$mbar. The film growth proceeded in the usual manner via the thermal decomposition of the metal-organic precursor. The decomposition mechanism to form stoichiometric ZnO was found to be promoted by the presence of the water vapour.

For deposition onto optical fibres (fused silica, 125μm diameter), a special sample holder 23 as illustrated in Figs. 3a and 3b was designed to fit the requirements arising from the fragile nature of this kind of substrate. Fig. 3a, illustrates a top perspective view of the sample holder while Fig. 3b illustrates a side perspective view. The requirements include:

i. fibres of a length of ~20cm to be secured during the vacuum transfer and;

ii. the holder enables expansion of the fibres during the deposition of 450°C.

Up to four fibres eg. 30, 31 are loaded into the ceramic tubes eg. 32 which have two cores of 250μm diameter each. The tubes eg. 32 are positioned so that the bottom edge of each core is level with the surface of the copper heating block 38. The fibres are pressed onto the cooper

heating block at one end by a copper clamp 39 fitted with a central screw 40 to ensure even pressure distribution on the fibres, with a minimum of two optical fibres in the holder being required. The surface of the polished copper clamp also provides a planar reference surface to control the crystallinity of the deposited film. X-Ray Diffraction (XRD) spectra taken from the copper clamp were used to estimate the degree of c-axis orientation in the deposited films. XRD patterns can not be obtained directly from the ZnO films deposited onto to the fibre, therefore, the obtained reference XRD spectra from the copper clamp can only be used as an indication whether the growth conditions were suitable for growing polycrystalline, c-axis oriented films onto planar substrates. Only one clamp 39 was used on the fibres to enable expansion of the fibres without creating intrinsic stress within the fibres during the deposition at 450°C. Fig. 4 shows a cross-sectional schematic view of the fibres eg. 31 mounted onto the copper heating block. One advantage of CVD growth was the non-directional growth aspects of the deposition process which enables depositions onto non-planar substrates without severe shadowing effects as obtained in sputter deposition techniques where the impulse of the impinging atoms is high. In CVD growth a high partial pressure of precursor in the vicinity of the heating block should allow for film growth onto every heated surface in the precursor vapour, since the kinetics of the precursor molecules in the gas phase can be described by random thermal movement.

Due to the fact that the fibres 31 are only clamped 39 onto the heating block 38 in the sample holder design, an air gap between bottom of the fibres and the surface of the heater will remain. The thickness of this air gap 50 can be expected to be in the order of the roughness of the materials pressed against each other, (estimated to be about 0.5μm). However, in the case of only one clamp 39 used in the designed sample holder, the upper limit for the

gap (denoted d) can be estimated to be $d=d_{core}-d_{fibre}$ from the geometry at the free end of the fibre on the heating block, neglecting any curvature of the fibre perpendicular to the surface of the heater 38 for the short length (1cm) between clamp 39 and ceramic end 44 in the design. With the diameter of the core, $d_{core}=250\mu m$ and the diameter of the fibre $d_{fibre}=125\mu m$, this upper limit is 125μm. Thus deposition of the ZnO film over 360° of the fibre surface without rotating of the fibres was possible. It was found experimentally, that the heater temperature range from 350°C - 450°C was suitable for the decomposition of the precursor on the fibre surface.

The ZnO films were deposited onto a ~15nm thick Cr contact layer which was sputter deposited onto the fibre at room temperature in a high vacuum sputter system. During Cr sputter deposition, the fibres were mounted in an aluminium frame which was rotated by 180° between two deposition cycles to coat the fibre around the full 360° due to the shadowing effect. For deposition of the top Cr contact onto the ZnO film, a mask was attached to the frame which restricts the deposition area to a length of 6mm centred on the film.

The ZnO films were characterised using X-ray diffraction (XRD) and X-ray photo-electron spectroscopy (XPS). The former technique was used to investigate the structural film properties of the ZnO films whereas the latter gave information of the chemical film composition. The XRD measurements were performed in a Siemens Kristalloflex diffractometer in air with an un-monochromated Cu Kα source and the XPS measurements in a VG ESCALAB 220XL ultra high vacuum analysis chamber equipped with a monochromated Al Kα source and a hemispherical electron energy analyser.

In Fig. 5, the obtained XRD spectra of a ZnO reference powder 60 (Aldrich, 99.9%) and of a CVD-grown film 61 onto

a planar SiO_2 substrate under ideal conditions are shown. In the reference powder, the ZnO crystallites are randomly oriented with respect to the azimuth of the planar sample holder. Thus all crystal planes e.g. 63-65 can be detected in XRD analysis. The chosen 2θ angle range between 30° and 38° is commonly used to characterise ZnO since it covers the strongest peaks in the overall spectra. In the XRD spectrum 61, taken from the CVD-grown film, only one peak 67 is present associated with diffraction from the (002) crystal plane. This indicates that the film crystallites are oriented with the c-axis perpendicular to the substrate/planar sample surface. This is the preferred orientation for piezo-electric applications since the piezo-electric effect is strongest along the polar crystal axis.

In Fig. 6, a XPS depth profile of a deposited ZnO film under identical conditions is shown. The atomic concentration of the film components is plotted as a function of sputter depth. At the outer surface of the film, the film composition differs from the 'bulk' in that an increased carbon contamination 70 and a decreased relative zinc concentration 71 is found. This can be explained by surface contaminations due to the exposure of the films to air after the film deposition. Such surface contaminations are mainly oxygen, hydroxides and hydrocarbons, giving rise to the obtained increased concentrations of oxygen and carbon at the film surface. In the deeper film layers, the film composition is that of stoichiometric ZnO with a carbon contamination level that is below the XPS detection limit.

The accuracy of the quantification method used can be controlled to the extent that the substrate composition measured after the ZnO film is completely removed is in agreement with the expected value for SiO_2 of 66.7% oxygen and 33.3% silicon. The above results suggest excellent chemical and structural properties of ZnO films deposited

onto planar substrates using the modified SSCVD process.

In Fig. 7, the XRD spectrum 80 of the film deposited onto the copper reference surface during the Zn deposition onto the optical fibres is shown. Again, only the one peak associated with the (002) plane is present, again suggesting that the deposition conditions were ideal. From scanning electron microscopy (SEM) images of the optical fibre with the deposited ZnO film, it was further evident, that the film was deposited over the full 360° range.

In Fig. 8, there is illustrated an experimental setup used to characterise the response of the ZnO phase modulator. A transducer 91 was spliced into one end 92 of a Mach-Zehnder interferometer constructed from two 50% single-mode couplers 93, 94. A 1553nm DFB laser diode 96 (coherence length > 10m) with isolator was used as the optical source. At the output of the interferometer a high speed (bandwidth >> 10GHz) photodetector 97 in conjunction with an RF spectrum analyser 98 (bandwidth 1.8GHz) was used to measure the amplitude of the optical modulation. A RF source 100 capable of delivering 700mW into 50Ω was used to drive the ZnO device 91 with the power monitored using an RF power meter 102 and a -20dB directional coupler 103. To maintain a constant state of quadrature during measurements, the DC portion of the interference signal from the MZI was used as a feedback 104 to control a drive compensator (thermal) 106 in the reference arm 107 of the interferometer.

When a sinusoidal drive voltage is applied to the modulator 91, the amplitude of the signal at the output 97 of the Mach-Zehnder interferometer may be expressed as:

$$P = \frac{P_{max}}{2}\,[1+\cos(\phi+\beta\sin(2\pi f_{mod}t)],$$

where P_{max} is the launched intensity, f_{mod} is the frequency of the drive signal and ϕ is the steady-state phase difference between the two arms of the interferometer (maintained constant by the feedback circuit). The

modulation index β is given by

$$\beta = \frac{2\pi}{\lambda} \Delta n L$$

where Δn is the peak change in effective core index λ = 1553nm is the wavelength, and L = 0.006m is the device length.

Equation 1 may be expressed as the sum of Bessel functions $J_n(\beta)$ which occur at harmonics of the drive signal frequency:

$$P = \frac{P_{max}}{2}[1+\cos(\phi+\beta\sin(2\pi f_{mod}t)]$$

$$= \frac{P_{max}}{2}[1+\cos\phi.\cos(\beta\sin(2\pi f_{mod}t)) \sin\phi\sin(\beta\sin(2\pi f_{mod}t))]$$

$$= \frac{P_{max}}{2}[1-J_0(\beta)\cos\phi-2J_1(\beta)\sin\phi\sin(2\pi f_{mod}t)] [+ 2J_2(\beta)\cos\phi\cos(4\pi f_{mod}t)-2J_3(\beta)\sin\phi\sin(6\pi f_{mod}t)] [-...$$

Using the ratio of the measured amplitudes of first and second sidebands $J_1(\beta)\cos\phi$ / $J_2(\beta)\sin\phi$, the modulation index β can be calculated knowing the phase relationship between the two arms of the interferometer.

Across the measured frequency range of 100 to 700MHz the device 90 exhibited a series of well defined resonances corresponding to the radial modes of the fibre-film composite. These maxima were separated by approximately 49MHz in agreement with the expected value for a 125μm fibre.

In Fig. 9, there is shown the measured phase modulation versus the square root of the driving power for two of the resonance frequencies at 283MHz and 478MHz. At 283MHz, an almost linear modulation efficiency of 0.17rad/$\sqrt{Mw}$ with a maximum phase shift of 3.5 radians was measured for a driving power of 580mW. Similar results of

0.14rad/$\sqrt{Mw}$ and 3.2 radians at 680mW were attained at 478MHz. Fig. 9 includes the data reported in N.H. Ky, H.G.Limberger, R.P. Salathe and G.R. Fox, "400MHz all-fibre phase modulators using standard telecommunications fibre", *in The Proceedings of conference on Optical Fibre communications 1996,* Feb.. 25 - Mar.1, 1996, San Jose, California, USA, (Ky et al.) for a comparable 6mm long device using a 6μm thick ZnO film deposited by sputtering measured at a frequency of 196.5MHz. Clearly, while the performance of Ky et al device is limited for input powers above 36mW, for the CVD device nonlinear effects are only evident at much higher input powers. In this region the obtained phase shift of approximately π radians which is optimum for switch and modulator applications has been achieved.

Previously, in the literature, device efficiency has been compared using the empirical figure of rad/$\sqrt{Mw}$ /*cm* of device length. In these terms of the preferred embodiment device efficiency of 0.28 rad/$\sqrt{Mw}$ /*cm* (at 283MHz) is approximately 35% higher than the previous most efficient device reported by Ky et. al. For the constructed modulator any saturation effects occur at much higher driving powers suggesting an excellent chemical film composition and structure of the CVD grown ZnO films.

Two aspects of how film thickness influences device performance may be considered. Firstly, for the same applied voltage, use of thinner films may enable higher electric fields in the device resulting in greater induced strain. Secondly, the elastic coupling between active film and fibre is also influenced by film thickness. The improved performance measured in the present device may therefore be related to a combination of film thickness and chemical composition.

In summary an all-fibre acousto-optic phase modulator has been developed using CVD grown ZnO films as the active

material. The CVD deposition technique allows 360° coating of the optical fibre without the need for fibre rotation. This significantly reduces the complexity in manufacturing all-fibre devices. The maximum phase shift measured for a 6mm long device at 283MHz was 3.5 radians at a drive power of 580mW. Unlike in previous designs using sputtered ZnO films the maximum attainable phase shift is not significantly limited by thermal and mechanical loss effects at higher driving powers. The measured efficiency of 0.28 rad/$\sqrt{Mw}$ /cm of device length is 35% higher than previously reported which may be the result of our relatively thin films (0.4-0.9μm).

It would be appreciated by a person skilled in the art that numerous variations and/or modifications may be made to the present invention as shown in the specific embodiment without departing from the spirit or scope of the invention as broadly described. For example, using the single source CVD method, depositions can be carried using a range of temperature conditions to produce similar quality films in addition to using other basic zinc compounds to grow films. For example, in Fig. 10 there is shown a plot of results obtained for ZnO films grown as a function of both precursor pressure and substrate temperature with the letters c or a indicating c or a axis orientation, c/r and a/r indicating predominantly c or a axis orientated with some random orientation and r indicating random orientation. The presented embodiment is, therefore, to be considered in all respects to be illustrative and not restrictive.

We Claim:

1. A method of manufacture of a substantially continuous circumferential coating on a non-planer substrate, said method comprising the step of:

utilising a substantially non directional gaseous deposition technique and a substantially static substrate deposition geometry to deposit said coating.

2. A method as claimed in claim 1 wherein the coating has piezo-electric modulation characteritics.

3. A method as claimed in claim 1 or 2 wherein the coating has electro-optic modulation characteristics.

4. A method as claimed in any one of the preceding claims wherein the coating has semiconducting properties.

5. A method as claimed in any preceedinng claims wherein the coating comprises substantially Zinc-Oxide.

6. A method as claimed in any one of the preceding claims wherein the non directional deposition technique comprises chemical vapour deposition.

7. A method as claimed in claim 6 wherein the non directional deposition technique comprises single source chemical vapour deposition.

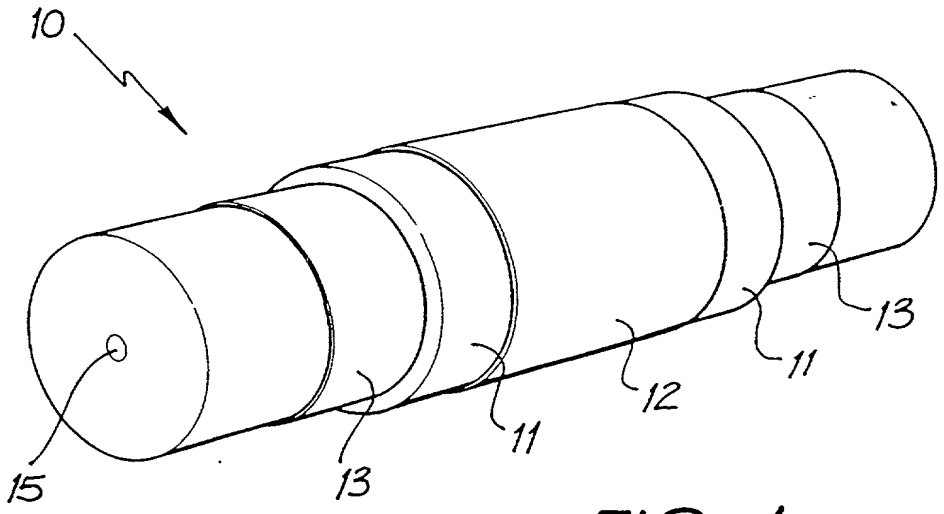
8. A method as claimed in any one of the preceding claims wherein the non-planar substrate is an optical fibre.

9. A method as claimed in claim 8 wherein at least one end of the optical fibre is clamped onto a substantially planar heating surface during the deposition.

10. A method as claimed in claim 8 wherein the optical fibre is clamped at a portion of the length of the fibre which is located at one end of a heating surface during the deposition.

11. A method as claimed in claim 8 wherein a movement of a free end of the optical fibre is limited to movement substantially along the axis of the optical fibre.

12. A receptacle for an optical fibre arranged to be used in a method of manufacture of a circumferential


10
15
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13

FIG. 1

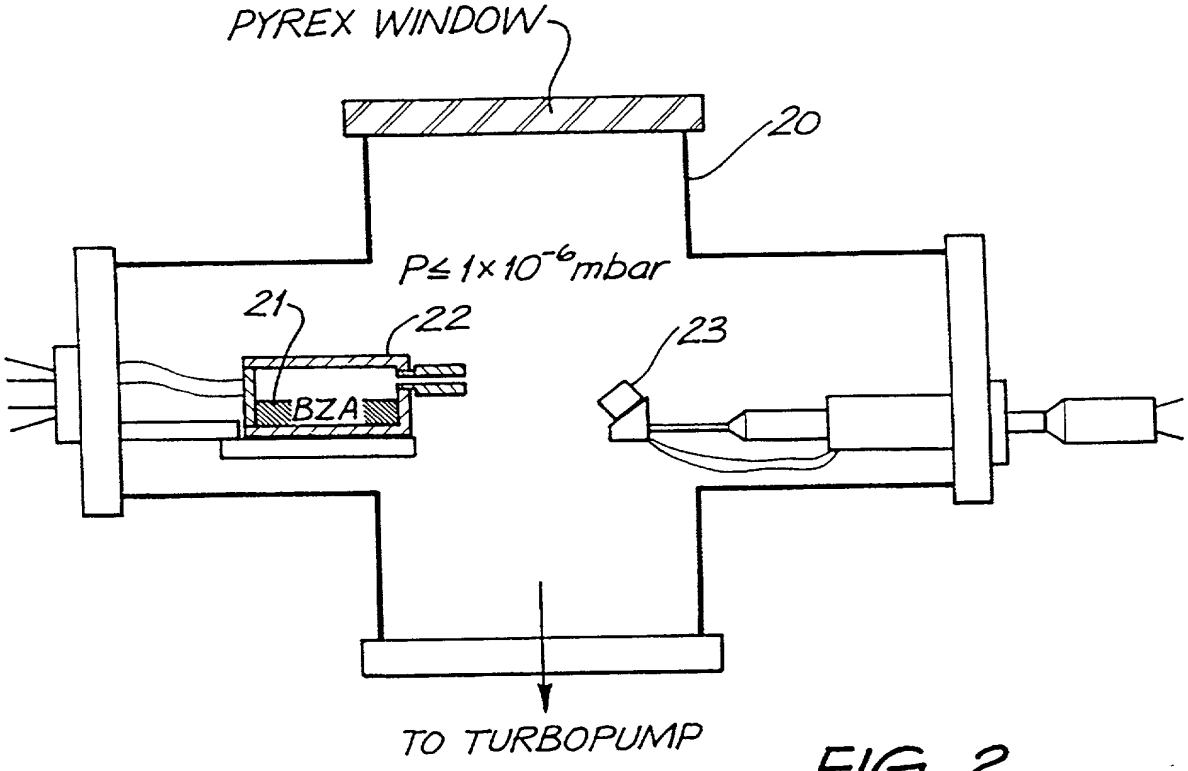
PYREX WINDOW
20
P≤1×10⁻⁶mbar
21
22
23
BZA
TO TURBOPUMP

FIG. 2

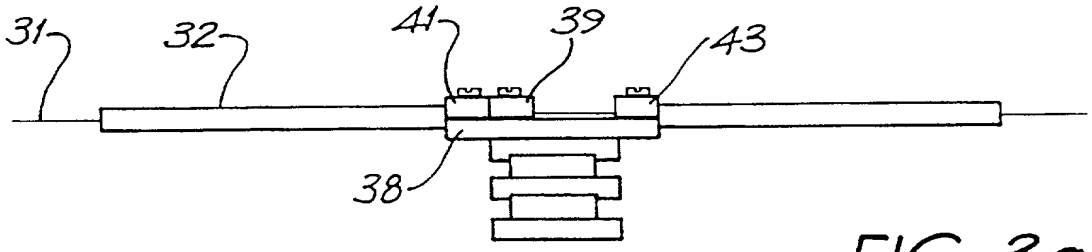

FIG. 3a

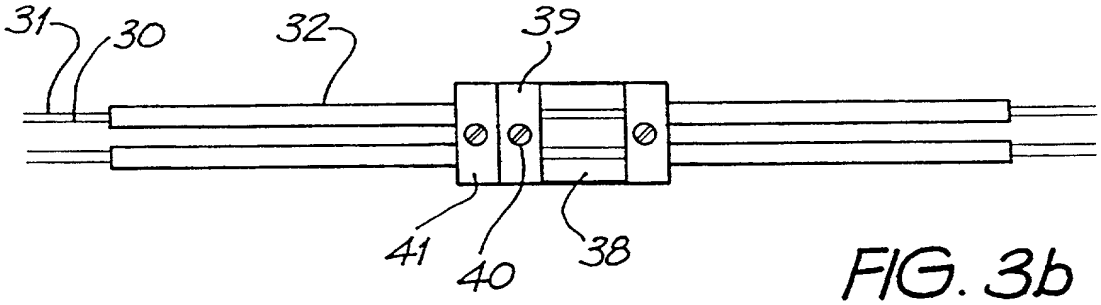

FIG. 3b

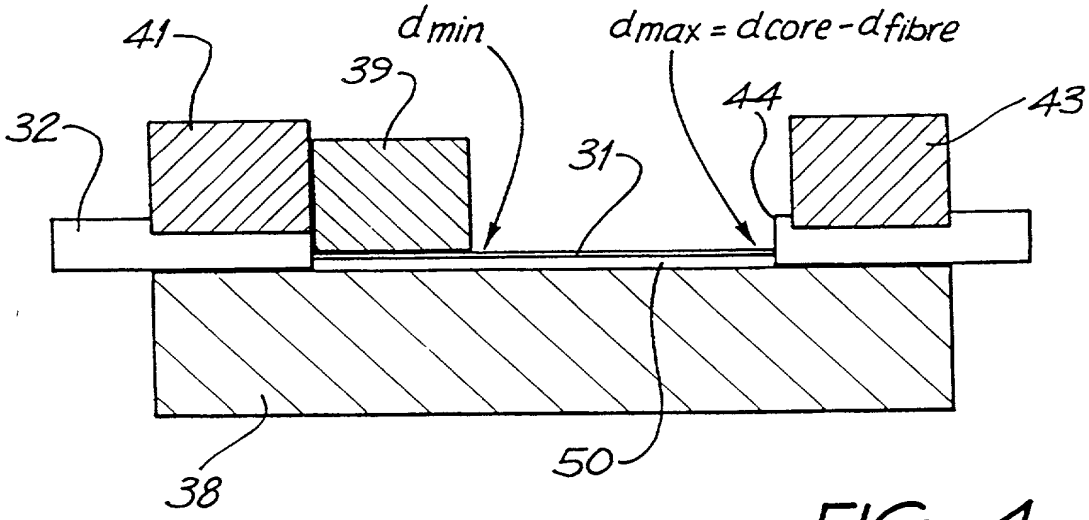

FIG. 4

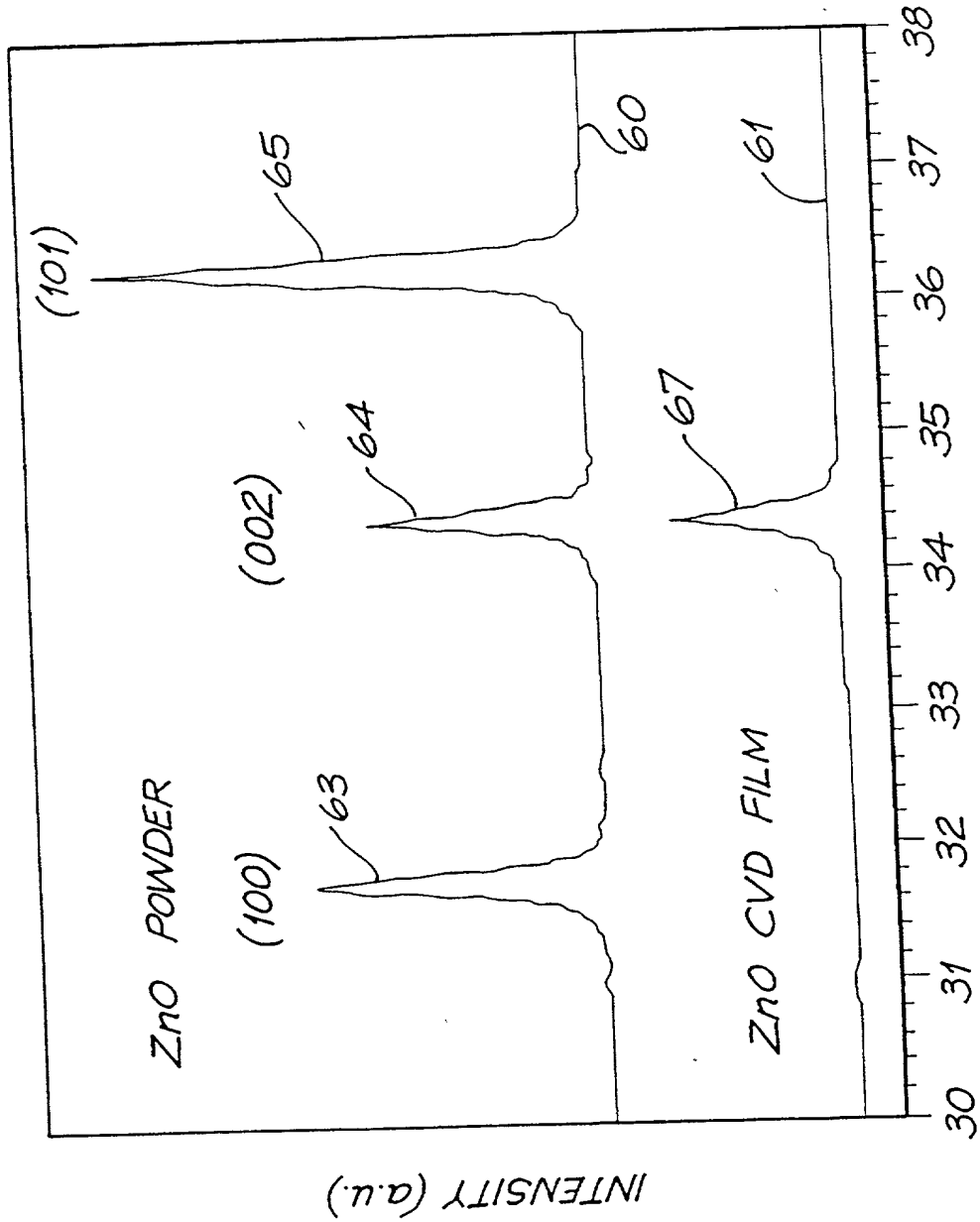
INTENSITY (a.u.)
ZnO POWDER
ZnO CVD FILM
(101)
(100)
(002)
63
64
65
60
61
67
30
31
32
33
34
35
36
37
38
2 THETA (DEG)

FIG. 5

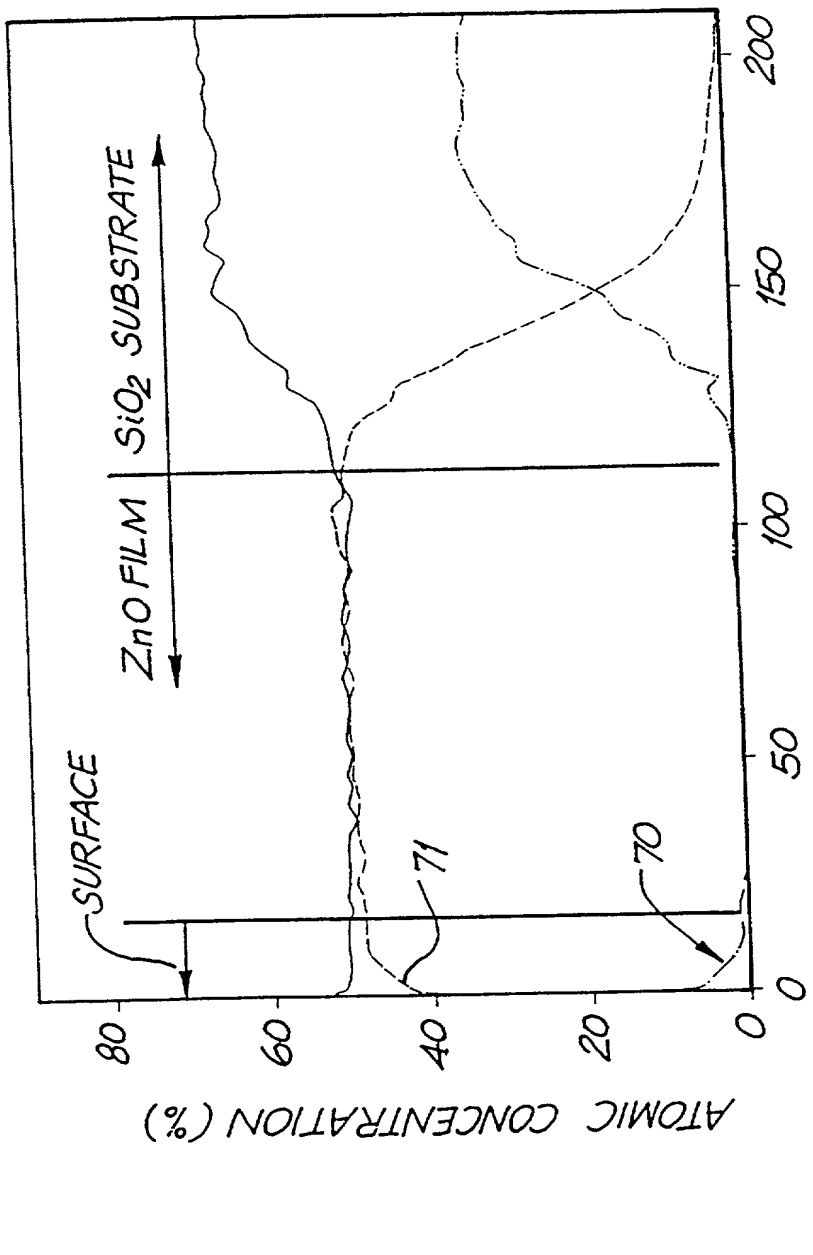
SURFACE
ZnO FILM
SiO2 SUBSTRATE
71
70
0
50
100
150
200
FILM DEPTH (nm)
0
20
40
60
80
ATOMIC CONCENTRATION (%)
CARBON
OXYGEN
SILICON
ZINC

FIG. 6

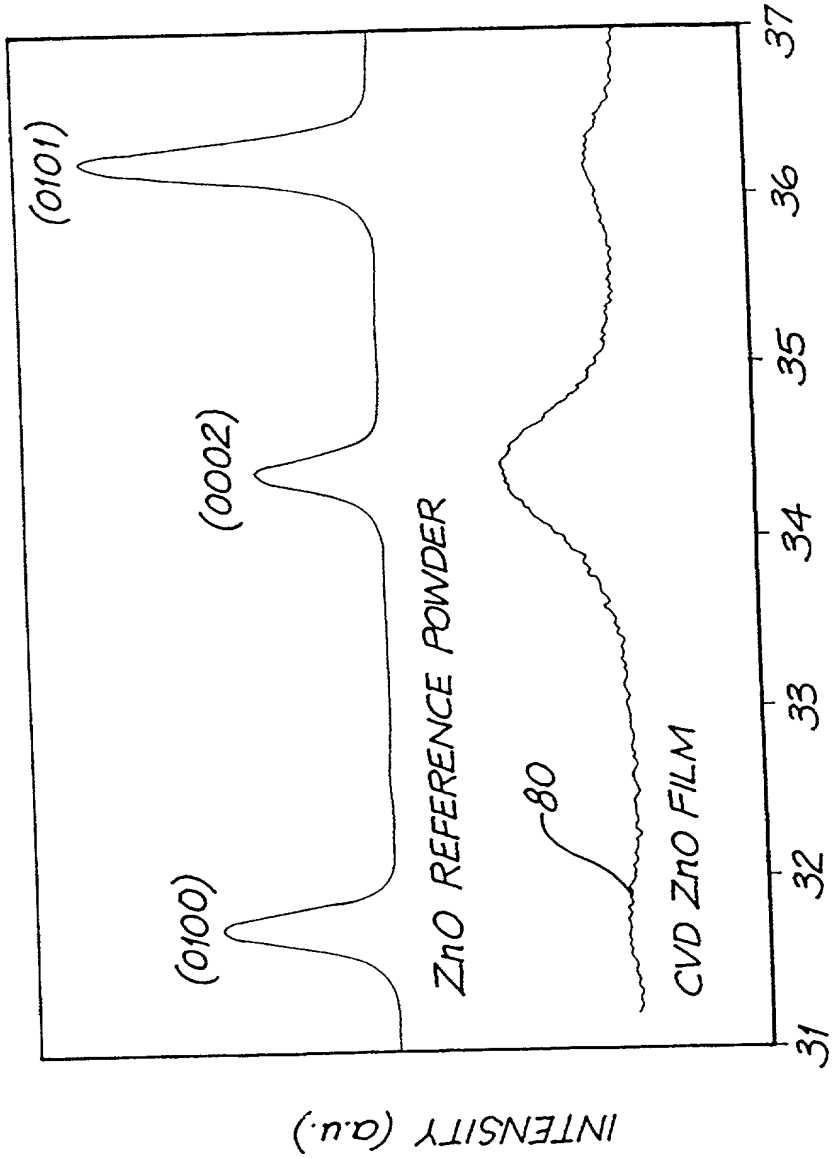
(0101)
(0002)
(0100)
ZnO REFERENCE POWDER
80
CVD ZnO FILM
31
32
33
34
35
36
37
2θ (DEGREES)
INTENSITY (a.u.)

FIG. 7

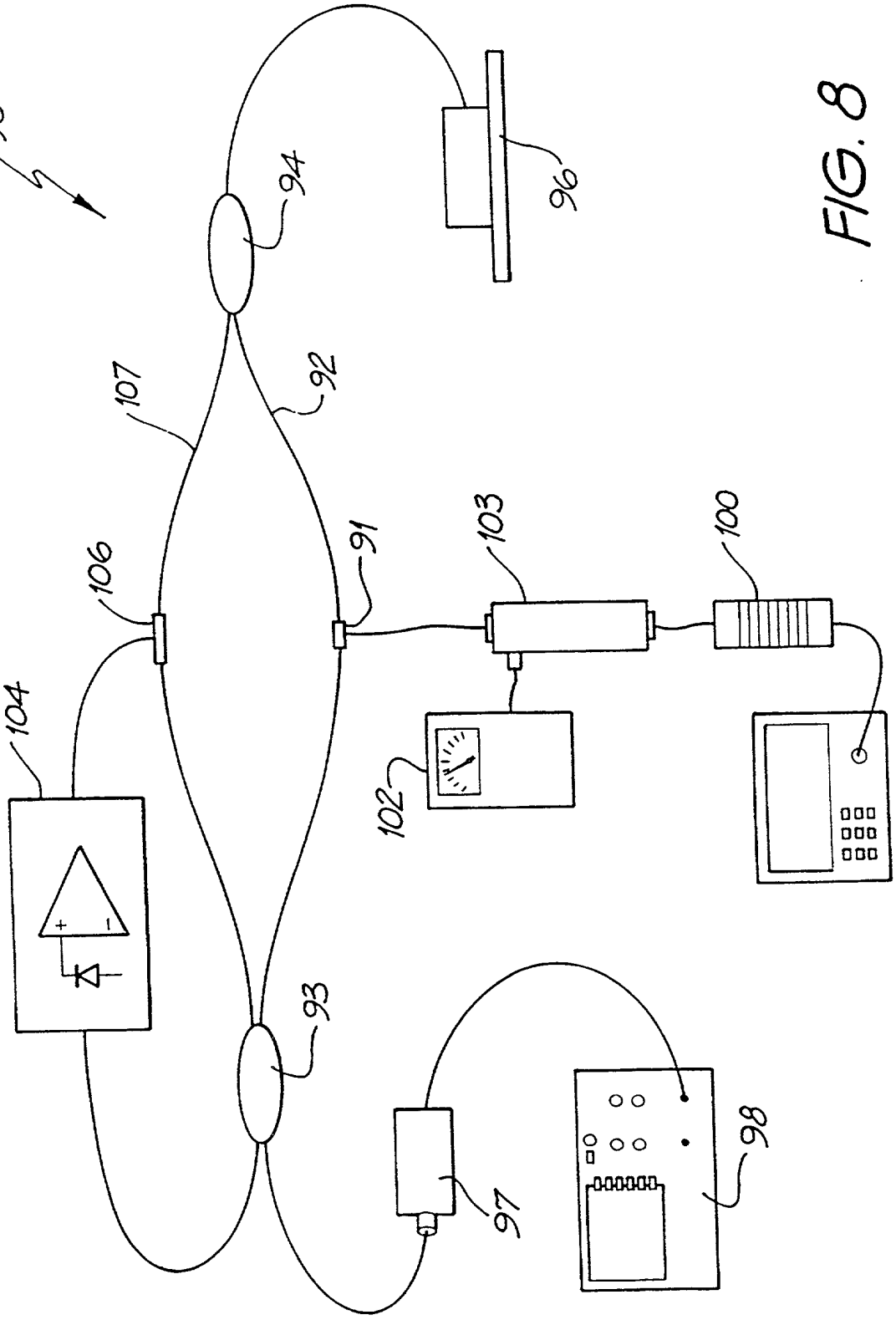

FIG. 8

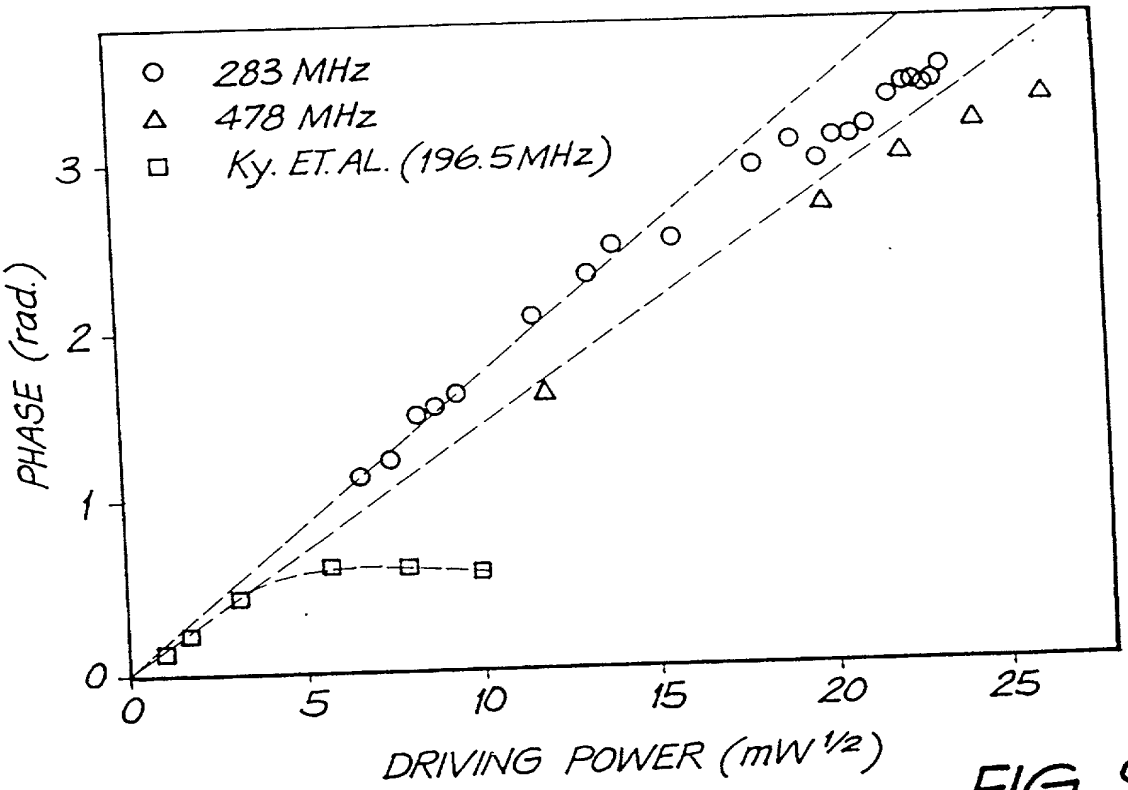
283 MHz
478 MHz
Ky. ET. AL. (196.5MHz)
PHASE (rad.)
DRIVING POWER (mW 1/2)
0
1
2
3
0
5
10
15
20
25

FIG. 9

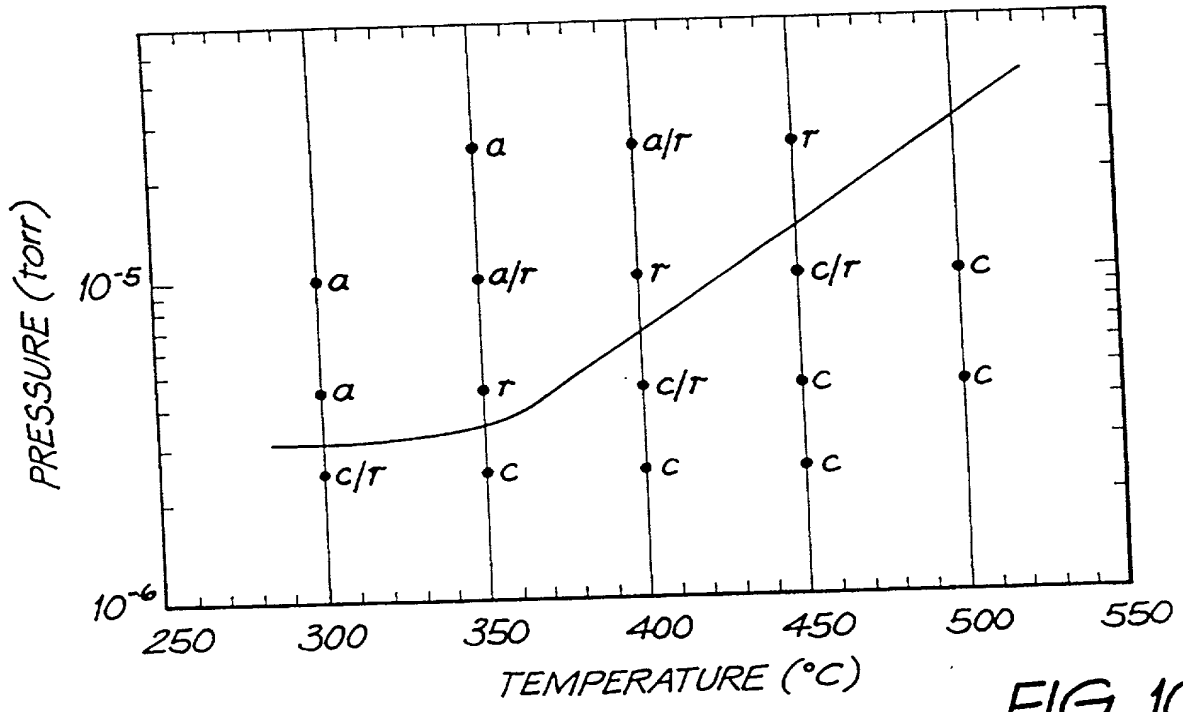
PRESSURE (torr)
10-5
10-6
TEMPERATURE (°C)
250
300
350
400
450
500
550
a
a/r
r
c/r
c

FIG. 10

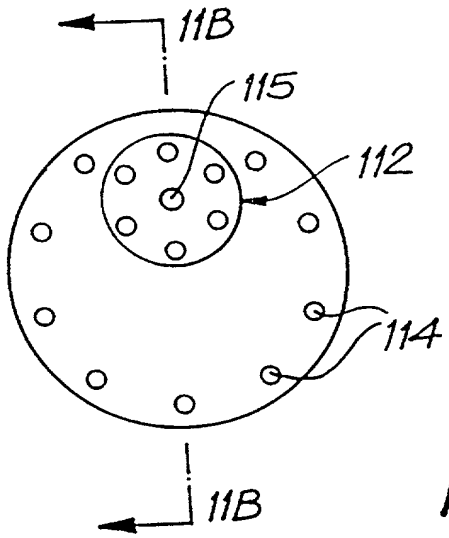

FIG. 11a

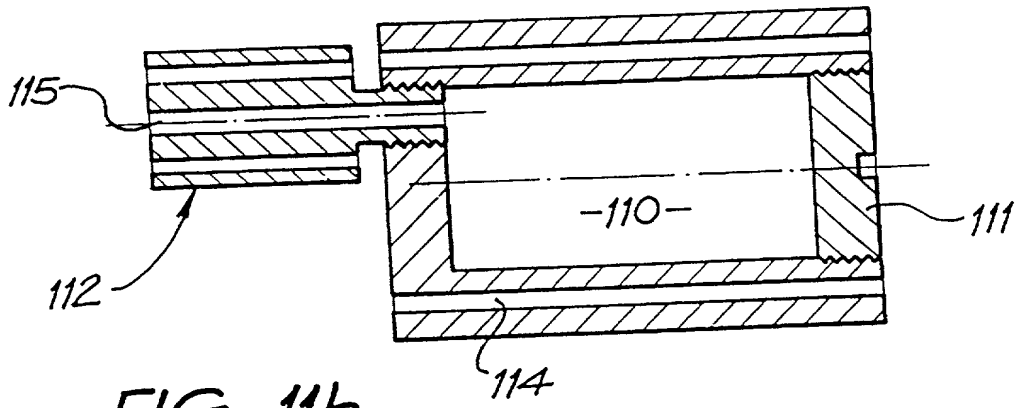

FIG. 11b

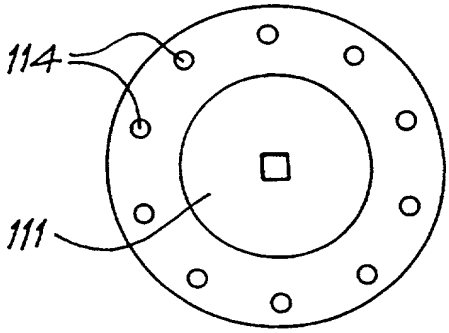

FIG. 11c

Atty. Dkt. No. ***054270/0122***

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I HEREBY DECLARE:

THAT my residence, post office address, and citizenship are as stated below next to my name;

THAT I believe I am the original, first, and sole inventor (if only one inventor is named below) or an original, first, and joint inventor (if plural inventors are named below or in an attached Declaration) of the subject matter which is claimed and for which a patent is sought on the invention entitled

FABRICATION OF ZINC OXIDE FILMS ON NON-PLANAR SUBSTRATES AND THE USE THEREOF

(054270/0122)

the specification of which (check one)

___ Is attached hereto.

XX Was filed on May 6, 1998 as United States Application Number or PCT International Application Number PCT/AU98/00326 and was amended on October 22, 1999, (if applicable).

THAT I do not know and do not believe that the same invention was ever known or used by others in the United States of America, or was patented or described in any printed publication in any country, before I (we) invented it;

THAT I do not know and do not believe that the same invention was patented or described in any printed publication in any country, or in public use or on sale in the United States of America, for more than one year prior to the filing date of this United States application;

THAT I do not know and do not believe that the same invention was first patented or made the subject of an inventor's certificate that issued in any country foreign to the United States of America before the filing date of this United States application if the foreign application was filed by me (us), or by my (our) legal representatives or assigns, more than twelve months (six months for design patents) prior to the filing date of this United States application;

THAT I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment specifically referred to above;

THAT I believe that the above-identified specification contains a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the invention, and sets forth the best mode contemplated by me of carrying out the invention; and

THAT I acknowledge the duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I HEREBY CLAIM foreign priority benefits under Title 35, United States Code §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number	Country	Foreign Filing Date	Priority Claimed?	Certified Copy Attached?
PO 6635	AUSTRALIA	06/May/1997	Yes	No

I HEREBY CLAIM the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

U.S. Provisional Application Number	Filing Date

I HEREBY CLAIM the benefit under Title 35, United States Code, §120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Application Number	Parent Filing Date	Parent Patent Number

I HEREBY APPOINT the following registered attorneys and agents of the law firm of FOLEY & LARDNER to have full power to prosecute this application and any continuations, divisions, reissues, and reexaminations thereof, to receive the patent, and to transact all business in the United States Patent and Trademark Office connected therewith:

ANKUR D. SHAH	Reg. No.	41,514
ANDREW E. RAWLINS	Reg. No.	34,702
ALAN I. CANTOR	Reg. No.	28,163
ARTHUR SCHWARTZ	Reg. No.	22,115
BETH A. BURROUS	Reg. No.	35,087
BARBARA A. MC DOWELL	Reg. No.	31,640
BERNHARD D. SAXE	Reg. No.	28,665
BRIAN J. DORINI	Reg. No.	43,594
BRIAN J. MC NAMARA	Reg. No.	32,789
CHARLES F. SCHILL	Reg. No.	27,590
COLIN G. SANDERCOCK	Reg. No.	31,298
AARON C. CHATTERJEE	Reg. No.	41,398
DAVID A. BLUMENTHAL	Reg. No.	26,257
DAVID P. OWEN	Reg. No.	43,344
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GEORGE C. BECK	Reg. No.	38,072
GEORGE C. BEST	Reg. No.	42,322
GEORGE E. QUILLIN	Reg. No.	32,792
GLENN LAW	Reg. No.	34,371
HAROLD C. WEGNER	Reg. No.	25,258
JAMES A. SPROWL	Reg. No.	25,061
JAYME A. HULEATT	Reg. No.	34,485
JOHNNY A. KUMAR	Reg. No.	34,649
JOHN J. FELDHAUS	Reg. No.	28,822
JOHN P. ISACSON, JR.	Reg. No.	33,715
KENNETH E. KROSIN	Reg. No.	25,735
LYLE K. KIMMS	Reg. No.	34,079
MICHAEL D. KAMINSKI	Reg. No.	32,904
MARY MICHELLE KILE	Reg. No.	35,217
MARVIN A. MOTSENBOCKER	Reg. No.	36,614
MICHELE M. SCHAFER	Reg. No.	34,717
MATTHEW R. COHEN	Reg. No.	40,960
MICHELLE S. MARKS	Reg. No.	41,971
PATRICIA D. GRANADOS	Reg. No.	33,683
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PHILLIP J. ARTICOLA	Reg. No.	38,819
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STEPHEN B. MAEBIUS	Reg. No.	35,264
SYBIL MELOY	Reg. No.	22,749
TODD J. BURNS	Reg. No.	38,011
THOMAS M. RIZZO	Reg. No.	41,272
WILLIAM T. ELLIS	Reg. No.	26,874

and I request that all correspondence be directed to:

FOLEY & LARDNER
Washington Harbour
3000 K Street, N.W., Suite 500
Washington, D.C. 20007-5109

Telephone: (202) 672-5300
Facsimile: (202) 672-5399

I UNDERSTAND AND AGREE THAT the foregoing attorneys and agents appointed by me to prosecute this application do not personally represent me or my legal interests, but instead represent the interests of the legal owner(s) of the invention described in this application.

I FURTHER DECLARE THAT all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Name of first inventor	Michael Herman KOCH
Residence	Erskineville, Australia AUX
Citizenship	AUSTRALIA
Post Office Address	85 Union Street, Erskineville, NSW 2043, Australia
Inventor's signature	Michael Koch
Date	16.12.1999

Name of second inventor	Robert Norman LAMB
Residence	Engadine, Australia
Citizenship	AUSTRALIA AUX
Post Office Address	9 Gamut Road, Engadine, NSW 2233, Australia
Inventor's signature	Robert Lamb
Date	26.12.1999

30 Name of fourth inventor	Gock Leong MAR
Residence	Lane Cove, Australia AUX
Citizenship	AUSTRALIA
Post Office Address	10/61 Helen Street Lane Cove NSW 2066
Inventor's signature	
Date	16/12/99

Name of third inventor	Peter Yorke TIMBRELL
Residence	Ontario, Canada CAN
Citizenship	CANADA
Post Office Address	12 Silver Aspen Crescent, Ottawa, Ontario K1B 3C3, Canada
Inventor's signature	
Date	

Atty. Dkt. No. ***054270/0122***

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(054270/0122)

the specification of which (check one)

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__XX__ Was filed on __May 6, 1998__ as United States Application Number or PCT International Application Number __PCT/AU98/00326__ and was amended on __October 22, 1999,__ (if applicable).

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Washington, D.C. 20007-5109

Telephone: (202) 672-5300
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Name of first inventor	Michael Herman KOCH
Residence	Erskineville, Australia AUX
Citizenship	AUSTRALIA
Post Office Address	85 Union Street, Erskineville, NSW 2043, Australia
Inventor's signature	
Date	

Name of second inventor	Robert Norman LAMB
Residence	Engadine, Australia AUX
Citizenship	AUSTRALIA
Post Office Address	9 Gamut Road, Engadine, NSW 2233, Australia
Inventor's signature	
Date	

3rd

Name of fourth inventor	Gock Leong MAR
Residence	Lane Cove, Australia AUX
Citizenship	AUSTRALIA
Post Office Address	10/61 Helen Street Lane Cove NSW 2066
Inventor's signature	
Date	

Name of third inventor	Peter Yorke TIMBRELL
Residence	Ontario, Canada
Citizenship	CANADA CAN
Post Office Address	P.T. 17 Silver Aspen Crescent, Ottawa, Ontario K1B 3C3, Canada
Inventor's signature	Peter Timbrell
Date	13/JAN/2000